METHOD AND APPARATUS FOR DEPOSITED FILM

BACKGROUND OF THE INVENTION

Field of the Invention

5   The present invention relates to a method for forming a deposited film and an apparatus for forming a deposited film, specifically to a film formation method and film formation apparatus for forming a thin film semiconductor and a photovoltaic element by, for

10   example, a plasma CVD method, and relates to a film formation method and a film formation apparatus for forming a semiconductor thin film of a photovoltaic element such as a solar cell, using amorphous silicon or an amorphous alloy. More specifically, the present

15   invention relates to a film formation method and a film formation apparatus for forming an amorphous silicon-based deposited film with a good and uniform quality in a large area while maintaining a high rate of film formation.

20   Related Background Art

By using amorphous silicon produced by the plasma CVD method, a semiconductor device having a large area can be comparatively easily formed as compared with use of crystal silicon or polycrystal silicon. Therefore,

25   many amorphous silicon films are used for semiconductor devices, each of which needs a large area, such as a solar cell, a photosensitive drum of a copying machine,

an image sensor of a facsimile, and a thin-film
transistor for a liquid crystal display.

Formation of an amorphous-silicon film is
generally conducted by a plasma CVD method in which a
raw material gas containing Si such as SiH_4 or Si_2H_6 is
decomposed with a high frequency discharge to change
the gas into a plasma state and form a film on a
substrate placed in the plasma.

When forming an amorphous-silicon film in a large
area by the plasma CVD method, a high frequency of RF
frequency (near 13.56 MHz) has been generally used
conventionally. However, in CVD apparatuses which each
have been developed for attempting to correspond to a
large area in response to requests from devices having
enlarged substrates, a problem of "non-uniformity of
film quality" which was in tolerance level in each
conventional apparatus corresponding to a small area
has become larger in recent years.

Moreover, since from a viewpoint of productivity
improvement acceleration of a film formation rate has
been also requested in connection with enlargement of a
substrate, several methods described below have been
performed.

Typical methods are:

(1) a method of increasing a flow rate of a raw
material gas such as SiH_4 or Si_2H_6,

(2) a method of increasing the electric power of a

high frequency discharge, and

(3) plasma CVD method using a VHF frequency
(about 30 to 300 MHz), which attract attention as
leading technology.

5   For example, it is reported in Amorphous Silicon
Technology 1992 p. 15-26 (Materials Research Society
Symposium Proceedings Volume 258) that, by making a
discharge frequency into a VHF frequency from a 13.56
MHz RF, a film formation rate can be markedly

10   increased, and the formation of a good deposited film
can be attained at a high rate.

However, in large area film formation, although
any one of the above-described methods is effective in
a point of increasing a film formation rate, they are

15   not effective in regard to the above-described
uniformity of film quality, and in addition, have
problems that they reduce the whole film quality and
the like.

20   SUMMARY OF THE INVENTION

Then, an object of the present invention is to
solve the above-described problems and to provide a
deposited-film formation method and a deposited-film
formation apparatus capable of forming an

25   amorphous-silicon-based deposited film with good
quality and good uniformity over a large area, at high
speed.

The present invention is to provide a deposited-film formation methods and deposited-film formation apparatuses as shown in the following items (1) to (20).

(1) A deposited-film formation method comprising the steps of: providing a discharge electrode in a vacuum vessel equipped with exhaust means; supplying a hydrogen gas and a raw material gas for a deposited film which contains at least an Si element (hereafter, the raw material gas including the hydrogen gas is referred to as "material gas"); supplying high frequency electric power to the discharge electrode to generate plasma from the material gas; and forming a deposited film on a substrate in the vacuum vessel by plasma CVD, the deposited-film formation method is characterized in that an auxiliary electrode is arranged in the plasma in the vacuum vessel, a periodically changing voltage is applied to the auxiliary electrode without causing a discharge to form a deposited film.

(2) The deposited-film formation method according to the above-described item (1), which is characterized in that a voltage applied to the above-mentioned auxiliary electrode has the maximum amplitude of 80 V or less.

(3) The deposited-film formation method according to the above-described item (2), which is characterized

in that the maximum amplitude of the above-described voltage is 20 V to 80 V.

(4) The deposited-film formation method according to the above-described item (2), which is characterized in that the maximum amplitude of the above-described voltage is 20 V to 60 V.

(5) The deposited-film formation method according to any one of the above-described items (1) to (4), which is characterized in that a voltage lower than the potential of plasma (plasma potential) from the above-described material gas is applied only in a certain period in at least one cycle of the periodically changing voltage when the periodically changing voltage is applied to the above-described auxiliary electrode.

(6) The deposited-film formation method according to any one of the above-described items (1) to (5), which is characterized in that one or more above-mentioned auxiliary electrodes are arranged at least in the flow direction of the above-mentioned material gas.

(7) The deposited-film formation method according to the above-described items (1) to (6), which is characterized in that a frequency of a high frequency electric power supplied to the above-mentioned discharge electrode is 10 kHz to 500 MHz.

(8) The deposited-film formation method according

to any one of the above-described items (1) to (7), which is characterized in that a frequency of a high frequency electric power applied to the above-described auxiliary electrode is equal to or more than 100 kHz.

5   (9) The deposited-film formation method according to any one of the above-described items (1) to (8), which is characterized in that the above-mentioned auxiliary electrode is an edgeless and small electrode having a small area facing a substrate in the

10   above-mentioned vacuum vessel.

(10) The deposited-film formation method according to any one of the above-described items (1) to (8), which is characterized in that the above-mentioned auxiliary electrode is formed from a round bar and the

15   like which is made to be small diameter and is made of a high strength material such as a high melting metal.

(11) A deposited-film formation apparatus for forming a deposited film on a substrate in a vacuum vessel by plasma CVD, which comprises a vacuum vessel

20   equipped with exhaust means, raw material gas supply means for supplying a raw material gas for forming a film and a discharge electrode for making plasma from the material gas, the raw material gas supply means and the discharge electrode being formed in the vacuum

25   vessel, and electric power introduction means for applying high-frequency electric power from a high frequency power source to the discharge electrode, the

deposited-film formation apparatus is characterized in that an auxiliary electrode is arranged between a substrate in the above-mentioned vacuum vessel and the above-mentioned discharge electrode provided with

5   facing the substrate and that the apparatus further comprises voltage application means which enables the application of a periodically changing voltage without causing a discharge.

(12) The deposited-film formation apparatus

10   according to the above-described item (11), which is characterized in that voltage application means for applying a voltage to the above-mentioned auxiliary electrode is formed so as to apply the voltage having a maximum amplitude of 80 V or less.

15   (13) The deposited-film formation apparatus according to the above-described item (12), which is characterized in that a maximum amplitude of the voltage is 20 V to 80 V.

(14) The deposited-film formation apparatus

20   according to the above-described item (12), which is characterized in that a maximum amplitude of the voltage is 20 V to 60 V.

(15) The deposited-film formation apparatus according to any one of the above-described items (11)

25   to (14), which is characterized in that voltage application means for applying a voltage to the auxiliary electrode is formed so as to apply the

voltage lower than plasma potential from the above-described material gas, only in a certain period in at least one cycle of the periodically changing voltage.

5   (16) The deposited-film formation apparatus according to any one of the above-described items (11) to (15), which is characterized in that one or more above-mentioned auxiliary electrodes are arranged at least in the flow direction of the above-mentioned

10   material gas.

(17) The deposited-film formation apparatus according to any one of the above-described items (11) to (16), which is characterized in that the high frequency power source for supplying high frequency

15   electric power having a frequency of 10 KHz to 500 MHz to the discharge electrode.

(18) The deposited-film formation apparatus according to any one of the above-described items (11) to (17), which is characterized in that voltage

20   application means for applying a voltage to the above-mentioned auxiliary electrode is formed so as to apply high frequency electric power having a frequency of 100 KHz or more.

(19) The deposited-film formation apparatus

25   according to any one of the above-described items (11) to (18), which is characterized in that the above-mentioned auxiliary electrode is an edgeless and

small electrode having a small area facing a substrate in the above-mentioned vacuum vessel.

(20) The deposited-film formation apparatus according to any one of the above-described items (11) to (18), which is characterized in that the above-mentioned auxiliary electrode is formed from a round bar having a small diameter or the like which is made of a high strength material such as a high melting metal.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing an example of the constitution of a deposited-film formation apparatus that can perform a deposited-film formation method according to the present invention;

Fig. 2 is a graph showing the result of investigation about the luminescence strengths of hydrogen radical and SiH radical with respect to the voltage amplitude applied to an auxiliary electrode, according to Example 1 of the present invention;

Fig. 3 is a graph showing the result of investigation about the luminescence strengths of hydrogen radical and SiH radical with respect to the voltage amplitude applied to an auxiliary electrode, according to Example 2 of the present invention;

Fig. 4 is a chart showing the relation between the plasma potential and the amplitude of the voltage

applied to an auxiliary electrode, according to Example
3 of the present invention;

Fig. 5 is a graph showing the result of
investigation about the luminescence strengths of

5   hydrogen radical and SiH radical with respect to the
potential difference between a square wave and plasma
potential, according to Example 3 of the present
invention; and

Fig. 6 is a schematic diagram showing locations of

10   an auxiliary electrode against a substrate, according
to Example 4 of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In embodiments of the present invention, it is

15   possible to form an amorphous-silicon-based deposited
film, having good quality and good uniformity over a
large area at a high rate of film formation by applying
the above-described constitution. This is on the basis
of a fact that the present inventors found after

20   performing various types of investigation. The fact is
that these problems relating to film quality is the
variation of a rate of hydrogen radical with respect to
a precursor of a deposited film formed from a gas
containing an Si element. In other words, it becomes

25   possible to reduce the deterioration of uniformity of
film quality and the degradation of film quality
occurring over an entire surface when high-speed film

formation is performed over a large area.

Next, these are described below in detail. First, in the above-described constitution, by arranging an auxiliary electrode in plasma in a vacuum vessel, and

5   applying a periodically changing voltage to the auxiliary electrode without causing a discharge, and forming a deposited film, it becomes possible to accelerate an electron in plasma to about 16 eV (energy for giving a hydrogen molecular a maximum

10 disassociation cross-sectional area) and to generate a hydrogen radical in high efficiency. At this time, the periodic change of electric potential is to prevent the regular formation of an ion sheath preventing the approach of electrons to the vicinity of the auxiliary

15 electrode. This makes it possible to realize stable and effective acceleration of many electrons that electrons are returned in the vicinity of the electrode and expelled from the electrode radially (in the radial direction). Here, the gist of "without causing a

20 discharge" is not to generate a discharge derived from electric power applied to the auxiliary electrode.

Nevertheless, when the maximum amplitude of the voltage applied exceeds 80 V, depending on a generation condition of plasma, discharge may occur in the maximum

25 voltage. Here, it is important to form an electrical field without a discharge, and owing to this, it becomes possible to accelerate electrons to the energy

"that can more effectively decompose hydrogen molecules". In other words, by not generating a discharge, it becomes possible to heat the electrode extremely little and to make current passing through

5   the electrode extremely little. Since this allows a form of an electrode to be simple and slender in the field of temperature and current, it becomes possible not to leave a trace of the electrode in a deposited film on a substrate even when the electrode is arranged

10   near the substrate.

In addition, by applying a voltage lower than the potential of plasma generated from the material gas only in a certain period at least in one cycle of the periodically changing voltage when the periodically

15   changing voltage is applied to the auxiliary electrode, it becomes possible to effectively accelerate electrons in minimum voltage amplitude with little disturbing existing plasma.

As commonly known, when a voltage is applied with

20   providing an electrode in plasma, when the voltage applied is higher than plasma potential, a sheath caused by electrons (electron sheath) is formed on an electrode surface, and when the voltage applied is lower than the plasma potential, a sheath caused by

25   ions (ion sheath) is formed. Because these sheathes are density distributions of space charges, these sheathes are accompanied with an electrical field, and

hence, if a potential difference voltages from plasma potential is equal to a field strength, when potential lower than the plasma potential is applied, this field strength becomes larger (this is based on mass

5   difference between an electron and an ion). Thus, if it is intended to give electrons large energy by this electrical field, it is effective to apply an electric potential lower than the plasma potential to the electrode. Nevertheless, if all the electrons near the

10   electrode are expelled due to application of this voltage (an ion sheath is formed), apparently, other electrons cannot approach the electrode because of the electric field after that, and hence energy impartation to electrons stops.

15   Therefore, here, this problem is solved by such periodic voltage application that electrons are returned to the vicinity of the electrode by returning the applied voltage nearly to the plasma potential, and again applying a voltage lower than the plasma

20   potential.

        Up to now, as disclosed in, for example, Japanese Patent Application Laid-Open No. 5-24992, and Japanese Patent Nos. 2819030 and 2819031, many attempts have been performed in which ion energy is controlled by a

25   steady-state electric field (an electrical field that is near to a DC current-like electric field and hardly changes) generated by arranging an electrode in plasma

and applying various types of electric power and
electric potential. However, there has been no attempt
like the present invention that a periodic electric
field is applied as means for accelerating electrons
5   that accelerates (imparting high energy) for generation
of hydrogen radicals. The present invention is clearly
different from conventional commonly known technology
in the point of efficiently generating hydrogen
radicals by imparting specific energy (to efficiently
10   discompose only hydrogen) only to electrons in a high
frequency electric field where ions cannot follow
(energy is not given to ions).

Furthermore, by arranging a plurality of auxiliary
electrodes at least in the flow direction of a raw
15   material gas, it becomes possible to correct a
concentration gradient that the quantity of hydrogen
radicals in the plasma changes from the upstream of the
gas to the downstream. It is considered that the
concentration gradient of hydrogen radicals in this
20   flow direction of the gas is caused by a lower electron
temperature of general plasma than the dissociation
energy of hydrogen molecules. In this case, because
the material gas containing an Si element has
dissociation energy equal to or less than the electron
25   temperature, it is possible to make the concentration
of precursors almost uniform over an entire region of
plasma by adjusting a gas flow rate and discharge

electric power.

Moreover, a frequency of high-frequency power
applied to the discharge electrode is set preferably at
10 KHz to 500 MHz, and more preferably at 1 MHz to 200

5   MHz as a range of frequencies that can effectively
decompose the material gas and can generate uniform
plasma over a large area. In other words, the
decomposition efficiency of the material gas is low in
the frequency lower than about 10 KHz, and it is

10   difficult to obtain uniform plasma over a large area
because of difficult discharge by an electrode at a
frequency higher than about 500 MHz.

In addition, as an waveform of the periodically
changing voltage which is applied to the auxiliary

15   electrode, an waveform such as a square wave or a
trapezoidal wave is suitable because it is essential
that a falling edge is sharp from the necessity of
accelerating electrons during change of the voltage of
the auxiliary electrode from nearly plasma potential to

20   lower potential.

Furthermore, as for a frequency of the voltage
applied to the auxiliary electrode at this time, its
lower limit is set to be preferably 100 kHz or higher,
and more preferably 1 MHz or higher so as not to induce

25   unnecessary movement of ions (high energization).

On the other hand, its upper limit is set to be
preferably 5 GHz or lower, and more preferably 500 MHz

or lower since the upper limit is a trapping frequency of an electron or lower.

Moreover, the maximum amplitude of the voltage applied to the auxiliary electrode is set to be 80 V or

5   lower. However, considering a fact that the maximum disassociation cross-sectional area of a hydrogen molecule is about 16 eV, and permeability of electric field into plasma and attenuation of a hydrogen molecule, the maximum amplitude of the voltage is set

10   to be preferably 20 V to 80 V, and more preferably 20 V to 60 V.

In addition, in order to maximize the number of electrons to be accelerated, potential difference between the maximum value of the applied voltage and

15   plasma potential is set to be preferably 20 V or less, and more preferably 5 V to 15 V.

Moreover, as a form of the auxiliary electrode herein, a round bar, a square bar, or a plate is conceivable. However, a form having an area that faces

20   a substrate and is as small as possible, having no edge, and having a small volume hardly causes an abnormal discharge, turbulence of gas flow, radiation of heat from the auxiliary electrode, and the like. Hence, a suitable form is the round bar and the like

25   having a diameter that is made to be as small as possible with using a high strength material such as a high melting metal.

Furthermore, the material gas is a gas including a compound that contains at least silicon atoms and can be gasified, or may contain a gas including a compound that contains germanium atoms and can be gasified, a

5 compound that contain carbon atoms and can be gasified or the like, or a mixed gas of the above-described compounds.

Concretely, as the compound that contains silicon atoms and can be gasified, a chain or cyclic silane

10 compounds are used. More concretely, the used compound includes gases or compounds that can be easily gasified, for example, SiH_4, Si_2H_6, SFH_3, SiF_2H_2, SiF_3H, Si_3H_8, SiD_4, $SiHD_3$, SiH_2D_2, SiH_3D, $SiFD_3$, SiF_2D_2, $Si_2D_3H_3$, $(SiF_2)_5$, $(SiF_2)_6$, $(SiF_2)_4$, Si_2F_6, Si_3F_8, $Si_2H_2F_4$, $Si_2H_3F_3$,

15 SCl_4, $(SiCl_2)_5$, $SiBr_4$, $(SiBr_2)_5$, Si_2Cl_6, $SiHCl_3$, SiH_2Br_2, SiH_2Cl_2, $Si_2Cl_3F_3$, and the like. Here, D denotes deuterium.

Concretely, the used compound that contains germanium atoms and can be easily gasified includes

20 GeH_4, GeD_4, GeF_4, $GeFH_3$, GeF_2H_2, GeF_3H, $GeHD_3$, GeH_2D_2, GeH_3D, Ge_2H_6, Ge_2D_6, and the like.

Specifically, the used compound that contains carbon atoms and can be easily gasified includes CH_4, CD_4, C_nH_{2n+2} (n is an integer), C_2H_2, CO_2, CO, and the

25 like.

Furthermore, atoms belonging to Group III and Group V of the Periodic Table (hereinafter, referred to

as "Group III atoms" and "Group V atoms", respectively)
can be used as a material to be introduced into a
p-type layer or an n-type layer in order to control
valence electrons.

5   As for materials effectively used as the starting
material for the introduction of Group III atoms,
concretely, a material for the introduction of boron
atoms includes boron hydride such as B_2H_6, B_4H_{10}, B_5H_{11},
B_6H_{10}, B_6H_{12} and B_6H_{14}, and boron halide such as BF_3 and

10   BCl_3. Besides, $AlCl_3$, $GaCl_3$, $InCl_3$ and $TiCl_3$ can be
included, too. In particular, B_2H_6 and BF_3 are
suitable.

As for materials effectively used as the starting
material for the introduction of group V atoms,

15   concretely, a material for the introduction of
phosphorous atoms includes phosphorus hydride such as
PH_3 and P_2H_4, and phosphorus halide such as PH_4I, PF_3,
PF_5, PCl_3, PCl_5, PBr_3, PBr_5, and PI_3. Besides, AsH_3,
AsF_3, $AsCl_3$, $AsBr_3$, AsF_5, SbH_3, SbF_3, SbF_5, $SbCl_3$, $SbCl_5$,

20   BiH_3, $BiCl_3$, and $BiBr_3$, can be included, too. In
particular, PH_3 and PF_3 are suitable.

Furthermore, it may be performed to adequately
dilute the above-described compound, which can be
gasified, with a gas such as H_2, He, Ne, Ar, Xe, or Kr

25   and introduce the mixture into a film formation
chamber.

Moreover, it is possible to use various kinds of

deposited-film formation apparatuses when a
deposited-film formation method herein is executed.
For example, an apparatus having the configuration
shown in the schematic diagram of Fig. 1 can be used.

5   The apparatus shown in Fig. 1 has the
configuration that a bar-shaped auxiliary electrode is
arranged between a substrate and a discharge electrode
facing the substrate, and a periodically changing
voltage is applied to the auxiliary electrode.

10   In Fig. 1, an electroconductive substrate 102 is
set on an electroconductive substrate holder 103 inside
a vacuum vessel 101, and is electrically grounded
together with the vacuum vessel. A heater 104 is
provided in the substrate holder 103, and the substrate

15   102 is heated to a predetermined temperature. A
plate-like discharge electrode 105 is provided in the
position facing the substrate 102, and a guard
electrode 106 is provided for the discharge electrode
105. A high frequency power source 107 is connected to

20   the discharge electrode 105 through a matching circuit
108 and a blocking capacitor 109. A high frequency
signal generator 112 is connected to the auxiliary
electrode 110 through a power amplifier 111.
Furthermore, in the vacuum vessel 101, a raw material

25   gas introduction pipe 115 connected to raw material gas
supply means 114 and an exhaust pipe 117 connected to
evacuation means 116 are provided for the introduction

and evacuation of the material gas. In addition, a valve 118 is provided in the exhaust pipe.

Hereinafter, examples of a formation method of an amorphous silicon-based deposited film by plasma CVD

5   according to the present invention are described, but the present invention is never restricted by these examples.

Example 1

In Example 1, a deposited-film formation apparatus

10   having the configuration shown in Fig. 1 was used, and a periodically changing voltage was applied to the auxiliary electrode 110. In addition, variation of the generated quantity of hydrogen radical (H*) and SiH* near a substrate with respect to the maximum amplitude

15   of the voltage was examined. Furthermore, this method was compared with a conventional deposited-film formation method that did not adopt an auxiliary electrode.

Hereinafter, according to production procedure, a

20   production method will be described in detail.

(1) In the apparatus shown in Fig. 1, first of all, a 30-cm square and 0.15-mm-thick stainless steel substrate 102 (SUS430-BA) was set in the substrate holder 103 made of stainless steel so as to be

25   grounded, and the vacuum vessel 101 was once vacuum-exhausted to 1 Pa or lower by the evacuation means 116.

(2) The internal pressure of the vacuum vessel 101

was maintained at 100 Pa by introducing 100 sccm of He

gas from the gas supply means 114 through the gas

introduction pipe 115 and adjusting the opening of the

exhaust valve 118 while continuously vacuum-exhausting.

5   (3) In a condition of the above-described (2),

the substrate 102 was heated at 300°C for about 60

minutes by the heater 104 in the substrate holder 103.

When the substrate 102 was heated fully and uniformly,

the introduction of He gas was stopped while

10   continuously heating, and the material gas from the gas

supply means was changed to a mixed gas of SiH_4 and H_2.

Setting conditions were 300 sccm of SiH_4 gas flow rate,

1200 sccm of H_2 gas flow rate, and 266 Pa of internal

pressure in the vacuum vessel 101.

15   (4) The 40-MHz 500-W high-frequency power was

supplied from the high frequency power source 107 to

the discharge electrode 105, which is made of aluminum

and faces the substrate 102 by 1.5 cm apart, through

the matching circuit 108 and blocking capacitor 109.

20   In addition, a stainless steel round bar (5 mm

diameter, 35 cm long) was used for the auxiliary

electrode, and was provided in the center between the

discharge electrode and substrate, in parallel to them,

and approximately orthogonally to gas flow.

25   Furthermore, a square wave having a frequency of 1 MHz

and a duty ratio of 50% was applied so that its maximum

voltage became lower by 5 V than plasma potential. By

generating a glow discharge in the vacuum vessel 101

through supplying high-frequency power, and

plasma-discomposing a raw material gas, an amorphous

silicon film was deposited on the substrate 102.

5   In addition, the surface potential of the

auxiliary electrode was measured with an oscilloscope

113. The quantity of hydrogen radicals near the

substrate was measured by monitoring the luminescence

at 656 nm in realtime with a plasma

10 spectroscopy-measuring instrument.

Fig. 2 is a graph showing the result of

investigation about the 656-nm luminescence strength

showing the quantity of hydrogen radical (H*) and the

414-nm luminescence strength showing the quantity of

15 SiH radical (SiH*) with respect to the voltage

amplitude applied to the auxiliary electrode. Fig. 2

shows relative values obtained by regarding the

luminescence strength of H* and SiH* without providing

the auxiliary electrode as 1.

20   It can be seen from Fig. 2 that it is possible to

control the quantity of H* without changing the

quantity of SiH* by using a deposited-film formation

method of the present example, that is, by setting the

voltage amplitude to 80 V or less.

25 Example 2

In Example 2, with using the same procedure as

that in Example 1 except that a frequency of

high-frequency power supplied to the discharge

electrode was 60 MHz (besides, the following conditions

are also different), variation of the generated

quantity of hydrogen radical (H*) and SiH* near the

5   substrate with respect to the maximum voltage amplitude

was investigated. Furthermore, this method was

compared with a conventional deposited-film formation

method that did not adopt an auxiliary electrode.

Different conditions:

10   Material gas: SiH_4: 300 sccm, H_2: 600 sccm

Pressure: 133 Pa

Fig. 3 is a graph showing the result of

investigation about the 656-nm luminescence strength

showing the quantity of hydrogen radical (H*) and the

15   414-nm luminescence strength showing the quantity of

SiH radical with respect to the voltage amplitude

applied to the auxiliary electrode. Fig. 3 also shows

relative values obtained by regarding the luminescence

strength of H* and SiH* without providing the auxiliary

20   electrode as 1.

It can be seen from Fig. 3 that it is possible to

control the quantity of H* without changing the

quantity of SiH* by using a deposited-film formation

method of the present example, that is, by setting the

25   voltage amplitude to 80 V or less.

Example 3

In Example 3, with using the same conditions and

procedure as those in Example 1, by changing the
potential difference between the plasma potential and a
square wave (frequency: 1 MHz, duty ratio: 50%, voltage
amplitude: 35 V) applied to the auxiliary electrode

5   (plasma potential - minimum potential: Fig. 4),
variation of the generated quantity of hydrogen radical
(H*) and SiH* near the substrate was investigated.

Fig. 5 is a graph showing the result of
investigation about the 656-nm luminescence strength

10   showing the quantity of hydrogen radical (H*) and the
414-nm luminescence strength showing the quantity of
SiH radical (SiH*) with respect to the potential
difference between the square wave and the plasma
potential (plasma potential - minimum potential). Fig.

15   5 also shows relative values obtained by regarding the
luminescence strength of H* and SiH* without providing
the auxiliary electrode as 1.

It can be seen from Fig. 5 that it is possible to
effectively generate H* without changing the quantity

20   of SiH* by using a deposited-film formation method of
the present example, that is, by setting the voltage
applied to the auxiliary electrode to a voltage lower
than the potential of plasma derived from the material
gas, in at least one certain period of one cycle.

25   Example 4

In Example 4, with using a deposited-film
formation apparatus having the configuration shown in

Fig. 1, a semiconductor film for a photovoltaic device which has n-, i-, and p-type semiconductor layers (hereinafter, referred to as "n, i, and p layers") stacked by depositing amorphous silicon film on a

5 stainless steel substrate in the same manners as those in Example 1. Formation conditions of each layer of a photovoltaic device (n, i, and p layers) are shown in Table 1. Furthermore, between formation processing of respective layers, the vacuum vessel had been fully

10 evacuated once, and thereafter was purged several times with a He gas.

After n, i, and p layers had been deposited under formation conditions shown in Table 1, the substrate on which a deposited film was formed was taken out from

15 the apparatus after cooling, and a 70-nm-thick ITO transparent conductive film was vapor-deposited on the entire surface of the deposited-film by a known vacuum deposition apparatus. Moreover, on the ITO film, a 0.1-mm-thick Ag collector electrode having 0.1-mm-wide

20 comb teeth pattern in 3-mm intervals are provided by screen-printing of a silver paste, and 100 photovoltaic devices each having a size of about 30 mm square were formed. In addition, the photoelectric conversion efficiency of 100 photovoltaic devices formed was

25 measured. Photoelectric conversion efficiency was obtained as an average of 10 samples that were orthogonal to a direction of gas flow at each of 10

points (samples) in the gas flow direction. Variation
in the gas flow direction was defined as (maximum value
- minimum value)/(maximum value + minimum value).

Locations of auxiliary electrodes for the
5   substrate are shown in Fig. 6. Variation in the flow
direction on each of these four auxiliary
electrode-setting experiments was obtained. The result
was shown in Table 2 as a ratio ((presence of auxiliary
electrode)/(absence of auxiliary electrode)) against
10   the variation (obtained with similar procedure) in the
flow direction in case of not providing the auxiliary
electrode. Moreover, in regard to each of the
above-described four examples, the average of
photoelectric conversion efficiencies and film
15   formation rates of 100 samples is obtained. The
results are also shown in Table 2 as each ratio
((presence of auxiliary electrode)/(absence of
auxiliary electrode)) of the averages of the
photoelectric conversion efficiencies and film
20   formation rates in the case of providing the auxiliary
electrode with respect to the case of not providing the
auxiliary electrode.

It can be seen from Table 2 that, with the
deposited-film formation method according to the
25   present example, that is, by arranging a plurality of
auxiliary electrodes at least in the flow direction of
the material gas, it becomes possible to realize the

uniformity of characteristics of a deposited film in the gas flow direction without causing the degradation of film quality in the entire surface of the deposited-film while maintaining a high rate of film formation.

As described above, according to the present invention, it is possible to form the amorphous-silicon-based deposited film having good quality and good uniformity over a large area at a high rate of film formation.

Table 1

Name of deposited film	n layer	i layer	p layer
Conductivity type and crystal form film thickness (nm)	n-type a-Si: 30	i-type a-Si: 300	p-type a-Si: 10
Flow rate (sccm) of material gas			
SiH_4	300	500	10
H_2	1000	1000	3000
PH_3	1	None	None
BF_3	None	None	0.1
Pressure (Pa)	133	133	133
Substrate heating temperature (C°)	300	300	300
High-frequency power (W)	500	500	1200
Frequency (Hz)	60	60	60
Potential applied to auxiliary electrode			
Waveform and duty (%)	Square waveform: 50	Square waveform: 50	Square waveform: 50
Frequency (MHz)	1	1	1
Voltage amplitude (V)	35	35	35
Potential difference between plasma potential (Vp) and maximum voltage applied (Vmax) (Vp - Vmax)(V)	5	5	5

Table 2

	Variation ratio in gas flow direction (presence of auxiliary electrode/absence of auxiliary electrode)	Average photoelectric conversion efficiency ratio (presence of auxiliary electrode/absence of auxiliary electrode)	Average film formation rate ratio (presence of auxiliary electrode/absence of auxiliary electrode)
Experiment A	0.667	1.12	1.06
Experiment B	0.117	1.25	1.10
Experiment C	0.711	1.05	1.04
Experiment D	0.592	1.14	1.09